

**Construction of the SCRIBES (Sensitive Cooled Resolved Ion BEam
Spectroscopy) Instrument for the Detection of Astrochemically
Important Molecular Ions**

Andrew Mills
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171 Roger Adams Laboratory
University of Illinois-at Urbana-Champaign

Introduction

A full understanding of how the universe works requires understanding chemical interactions on all spatial scales. Many regions of space have unusual conditions compared to Earth, such as low density ($100\text{-}1 \times 10^6 \text{ cm}^{-3}$)¹ and temperature², and chemistry dominated by cosmic-ray ionization, which leads to higher relative abundances of ions than are found on Earth. In order to know the spatial and density distribution of molecules in space, one must search using radio, infrared, or optical astronomical observations. High resolution spectroscopic studies must be performed to obtain the molecular constants of the molecule, and thereby insight to the structure of the molecule. Such studies are challenging because these species are reactive and difficult to produce in quantities large enough to study.³

The first obstacle is producing ions in abundance. Plasma discharges can produce ion densities on the order of 10^{10} cm^{-3} .⁴ However, these molecular ions are produced in low concentrations compared to the neutral molecules present.⁵ Because neutral molecules are often 10^6 times more abundant than the ion of interest, techniques able to discriminate against neutrals are necessary. Although velocity modulation can discriminate against neutrals in a plasma, there are drawbacks to this technique. Most importantly, plasma discharges produce ions with high rotational and vibrational temperatures, adding spectral complexity and reducing the absorbance depth by diluting the population over many quantum states. As a result, ions probed by velocity modulation have been “hot” ions, with congested spectra, broad linewidths and weak absorbance. Consequently, analysis by high-resolution spectroscopy on larger carbo-cations (CH_5^+ , C_2H_5^+ , C_3H_3^+ , C_6H_6^+ , C_6H_7^+ , *etc.*) with velocity modulation is difficult. Therefore, a method which cools the ions after their production is necessary. By producing ions in a plasma, and then expanding the ions in a supersonic expansion, the rotational and vibrational

temperatures are lowered, thereby drastically simplifying the spectrum.^{6,7,8} However, the expansion still contains an overabundance of neutrals to ions. Although plasma conditions can be altered to shift the equilibrium towards certain ions, there is no spectroscopic discrimination against the background neutrals.

Ideally, a technique could be developed that both cools and separates the ions from the neutrals. One way to do that is to revisit the DLASFIB (Direct Laser Absorption Spectroscopy in a Fast Ion Beam) method pioneered by the Saykally group at Berkeley.^{9,10,11} This method involved using an uncooled cold cathode DC gas discharge source, where the anode discharged to a cathode that is biased above ground. Ions were created above ground potential, at the voltage of the cathode (V_{beam}). As the ions moved from the higher potential to ground potential, they were accelerated, and the spread of the longitudinal velocities and the linewidth were reduced, in a process known as kinematic compression.¹²

The fast ion beam was then collimated using electrostatic ion optics and turned 90° with an electrostatic quadrupole, effectively separating the ions from some of the neutrals. After separation, the ions were probed via direct laser absorption and identified using mass spectrometry. Saykally's method allowed for precise measurements as they were able to obtain linewidths of 20-40 MHz. The Saykally group was unable to successfully integrate supersonic cooling with their ion beam. As a result, the direct laser absorption technique was not sensitive enough to detect larger molecular ions due to high rotational and vibrational temperatures, as well as low density in the beam.

In the McCall group, we are working on building an improved version of DLASFIB, which we call SCRIBES (Sensitive Cooled, Resolved, Ion BEam Spectroscopy). The two major improvements of SCRIBES over DLASFIB are implementing a supersonic source to

adiabatically cool the plasma discharge and using continuous-wave cavity-ringdown spectroscopy¹³ (cw-CRDS) for more sensitive detection. Difference frequency generation (DFG) is used to provide a broadly tunable, robust laser. A time-of-flight mass spectrometer will also be used to collect mass spectral information. By monitoring the ions produced in the plasma, one can adjust the plasma conditions to increase the relative abundance of the ion of interest.

Progress on the SCRIBES instrument:

I have constructed an uncooled cold cathode source capable of producing a 30 μA beam of N_2^+ , using a backing pressure of 3.3 torr N_2 , a discharge voltage of 3.5 kV, and a beam voltage of 4.0 kV. A schematic of the source and electrostatic optics is given in Figure 1 and a schematic of the complete SCRIBES instrument is shown in Figure 2. Two electrodes were connected by a threaded piece of glass; the anode was an Ultra-Torr® fitting and the cathode was threaded onto the end of the glass with a silicone o-ring. The output of the power supply providing the float voltage (V_{beam}) was connected to the ground of the power supply providing the discharge voltage.

Electrostatic ion optics were constructed using the rod-mount design, including an asymmetric lens and an Einzel lens to control the beam size and reduce divergence. An electrostatic quadrupole¹⁴ was constructed, capable of turning the ion beam by 90°, yielding a 3 mm diameter beam. As the neutrals are unaffected by the electric field, they pass through without being turned, whereas the ions are turned into a drift region and effectively separated from the more abundant neutrals.

A high finesse ringdown cavity was built around the drift region to record the absorption of the ions in the beam. As there is a finite distance that the ions may traverse, there is also a

finite time during which the laser and ions interact, leading to a transit-time broadening. Figure 3 compares the reduced linewidth due to kinematic compression with the transform limited linewidth, and shows that the transform limit may begin to dominate the accelerated linewidth above float voltages of 4 kV. The transform limit linewidth can be lowered by eventually increasing the overlap region length.

Sensitive absorbance measurements can be made with cw-CRDS. The CRDS technique we use was originally developed by Romanini *et al.* A laser is passed through an acousto-optic modulator (AOM), and lenses match the size of the first-order diffracted beam to that of a high-finesse ringdown cavity. A piezoelectric transducer is used to dither the position of one of the cavity mirrors, thus changing the cavity length by at least one free spectral range. As the cavity length approaches resonance with the laser frequency, there is a buildup of the power within the cavity, and light begins to leak out of the cavity onto a detector. Once the detector output reaches a threshold value, the AOM is turned off and the incident light is diverted away from the cavity. The light contained in the ringdown cavity slowly leaks out at a rate proportional to the intrinsic cavity loss and any absorbing species. The resulting exponential decay is recorded, and fit to extract the characteristic time constant, which can then be related to the absorbance of the ions in the cavity.

As the laser propagates both parallel and anti-parallel to the ion beam, a Doppler splitting of the lines is observed. This splitting depends on the mass of the ion and the float voltage, allowing for confirmation of the species of interest. Thus, although the ion optics and quadrupole are unbiased with respect to mass, the spectroscopy can discriminate different absorbing species.

Currently a cold cathode serves where a supersonic source will eventually function. Therefore a supersonic discharge source will need to be designed. The pumps for differential pumping are available, however the system has no skimmer. Therefore the skimmer must also be planned. The conceptual design of the mass spectrometer has been completed, and is being converted into drawings for construction.

Difference Frequency Laser

In order to obtain high-resolution CRD spectra, a reliable laser with a narrow linewidth, broad tunability¹⁵, and a good transverse-mode profile is needed. There is no robust gain medium with wide tunability that allows for lasing in the 2-5 μm region.¹⁶ Although high-power cw-OPO's can be constructed, they are very difficult to develop and maintain.^{15,17} Difference frequency generation (DFG), however, allows for broad tunability, narrow linewidths, and good mode characteristics.¹⁸

The DFG process is described by $\omega_3 = \omega_1 - \omega_2$,¹⁹ and is possible only in materials with a non-zero second order nonlinearity susceptibility.⁶ Of the many nonlinear processes available, energy conservation and phase matching are used to amplify only the DFG process. Perfect phase matching can occur for a specific wavelength and temperature, however it is not possible for a wide range of wavelengths. Quasi-phase matching (QPM), is able to amplify non-linear processes at a wide range of frequencies and is accomplished by periodically poling the induced dipoles of an anisotropic crystal.²⁰ The quasi-phase matching occurs when the poling period (Λ) is chosen to satisfy a relation between the wavelengths and indices of refraction:²⁰

$$\Delta k = 2\pi \left(\frac{n_1}{\lambda_1} - \frac{n_2}{\lambda_2} - \frac{n_3}{\lambda_3} - \frac{1}{\Lambda} \right) = 0$$

A schematic of the completed DFG system is shown in Figure 4, and is similar to that used by Cao *et al.*²¹ A tunable cw-Ti:Sapph ring laser is made collinear with a cw-Nd:YAG laser and passes through a broadband anti-reflection coated short focal length achromat. As the YAG produces light with a different divergence than the Ti:Sapph, a telescope must be used to match the divergence of the two beams, so that they focus to the same place and size in the crystal. Following alignment, the proper temperature is found from the phase matching curve (Figure 5) and the IR light is detected with a LN₂ cooled InSb detector. Upon completion, laser power measuring 600 μW was successfully produced, which is similar to the power of the DFG constructed by Cao *et al.*²² who obtained 50 μW. Recently, the ability of our DFG coupled with our cw-CRDS has been demonstrated. Figure 6 shows the preliminary results of using 3.6 micron light to perform cw-CRDS in a pulsed H₃⁺ supersonic discharge source.

Future work:

Estimation of Instrument Sensitivity

Sensitivity calculations for the expected spectroscopic strengths of SCRIBES are shown in Figure 7. By comparing the estimated absorption strength for three molecules to the noise of the instrument, one observes that the signal-to-noise ratio is high enough to detect both a molecular ion of interest (C₃H₃⁺) and diagnostic molecular ions (H₃⁺ and N₂⁺). As the expected signal to noise is much larger for N₂⁺, we will use N₂⁺ to characterize the ion beam.

Ion Beam Spectroscopy Diagnostics with N₂⁺

A ringdown spectrometer is being coupled to the ion beam to evaluate the attainable linewidths. A tunable diode laser is modulated with an AOM and matched to a cavity. This project will help me develop a procedure for overlapping the ion beam with the laser and maximizing signal. This will demonstrate the achievable linewidth of the system, sensitivity of

the spectroscopy, and give us an uncooled source temperature. The spectroscopy will focus on the N_2^+ 1-0 band of the $A^2\Pi_u-X^2\Sigma_g^+$ system.

Implementation of Second Quadrupole and Mass Spectrometer

The use of a fast ion beam makes mass analysis quite challenging. As ions accelerated through several kV attain velocities on the order of 10^5 m/s, typical mass spectrometers (quadrupoles, Wien filters) become ineffective as a means of mass analysis. Bulky, heavy, expensive magnets are undesirable; precluding the use of magnetic sectors or ion cyclotron resonance (ICR) instruments. Time-of-flight instruments, however, are well known for their simplicity, ruggedness, and rapid data acquisition rate.²³ Although their resolution is lower than that of magnetic sectors, quadrupoles, and ICR, for our application, time-of-flight was chosen because it has sufficient resolution, and is cheaper.

After being turned again by 90° , the ion beam will be collimated again with a single Einzel lens. The continuous-wave ion beam will be pulsed using electronics with a fast rise-time. The pulsed beam will then be decelerated using a re-referencing technique²⁴, which allows the mass separation to occur in a shorter distance. Briefly, ions are passed through a tube held at a potential comparable to that of the float potential. This forces the ions to convert their velocity to potential energy. While the ions are inside this conductor, the potential on the tube is rapidly dropped to ground. Because the ions do not experience the force of the changing potential, the ions experience no acceleration as they leave the tube, at a reduced velocity and ground potential. This method allows us to maintain the narrow line widths from acceleration, the high resolution from a cw radiation source, and still achieve fast, high resolution mass analysis. The design for the mass spectrometer is outlined in Figure 2.

Spectroscopy of c-C₃H₃⁺

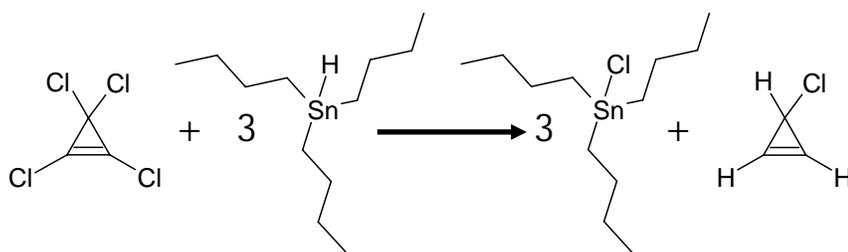
The cyclopropenyl cation (C₃H₃⁺) is one molecular ion of astrochemical importance²⁵ that can be studied with the SCRIBES instrument. C₃H₃⁺ is the smallest aromatic cation and is the dominant ion in acetylene and benzene flames, representing about 80% of the ion signal in these flames.²⁶ As a small aromatic molecule, calculations modeling aromaticity can be performed to high theoretical levels. Having structural data would allow one to evaluate the quality of these studies. C₃H₃⁺ is a good spectroscopic target because as a symmetric top it has a well characterized type of spectrum. Theoretical groups have calculated the molecular, electronic, and vibrational structure of C₃H₃⁺. Although it has been studied in a solid neon matrix,²⁷ and with N₂-ligands,^{28,34} no gas phase spectrum of bare c-C₃H₃⁺ has yet been recorded.²⁸

C₃H₃⁺ is an important ion for the interstellar medium (ISM). A probable mass-spectrometric detection of C₃H₃⁺ was found on the Giotto spacecraft mission to Halley's comet in 1986.²⁹ C₃H₃⁺ is also assumed to be the major precursor for c-C₃H₂, a ubiquitous molecule in the ISM.³⁰ Additionally, C₃H₃⁺ may be among the stable end products of reactions likely found in Jupiter's stratosphere.³¹ A tentative identification of c-C₃H₃⁺ in the stratosphere of Jupiter could be confirmed if high-resolution laboratory measurements of the vibrational transitions are made.³²

C₃H₃⁺ is an oblate symmetric top with D_{3h} symmetry. The most intense IR active mode of C₃H₃⁺ is the degenerate (ν₄) CH stretch.²⁵ Similar to CH₃⁺,³³ this band will have missing K=0 even J levels in the ground state, because of the nuclear spin statistics of having three interchangeable protons. Using rotation constants calculated by Lee *et al*, a band origin obtained experimentally from Dopfer *et al*,³⁴ and a Coriolis constant (ζ) obtained for CH₃⁺ by Oka *et al*,³⁵ a simulated spectrum (see Figure 8) was produced using the spectral simulation program

Pgopher.³⁶ This spectrum will assist us in knowing where to look in frequency space, what type of spectrum to expect and aid in line assignment.

We believe $C_3H_3^+$ can be produced through Penning ionization in our discharge plasma source from a likely precursor, C_3H_3Cl .³⁷ This molecule can be synthesized by successive reductions with tri-n-butyl tin hydride from perchlorocyclopropene as detailed by Breslow³⁸. As mild DC plasmas are able to ionize t-butyl chloride to the tertiary carbocation,³⁹ we expect the aromatically stabilized cation to be even more stable.



Summary

Astronomical observations can identify molecules and ions in the ISM. Before these species can be detected, high resolution studies must first be performed. Some problems associated with high resolution spectroscopy of ions have been discussed, as well as some suggested improvements with the SCRIBES system. In particular, the supersonically cooled fast ion beam will yield highly resolved spectra of rotationally and vibrationally cooled ions. By separating the ions from the neutrals using ion optics and DC quadrupoles, the spectra are simplified. Using continuous-wave cavity ringdown spectroscopy will yield sensitive and high resolution spectra. The construction of a time of flight mass spectrometer will enable real time monitoring of ion production and allow us to tweak the plasma to produce ions of interest more efficiently. I have shown that our system should be sensitive enough to record high resolution

spectra for $C_3H_3^+$, and have presented a simulated spectrum. Finally, the construction of our widely tunable difference frequency generation laser has been described.

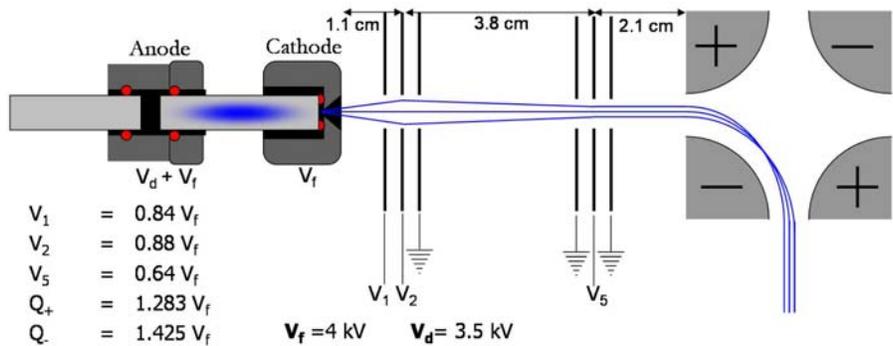


Figure 1 N_2^+ ion source (uncooled-cold cathode), asymmetric and Einzel lens, electrostatic DC quadrupole; used for creating, focusing and turning the ion beam by 90° .

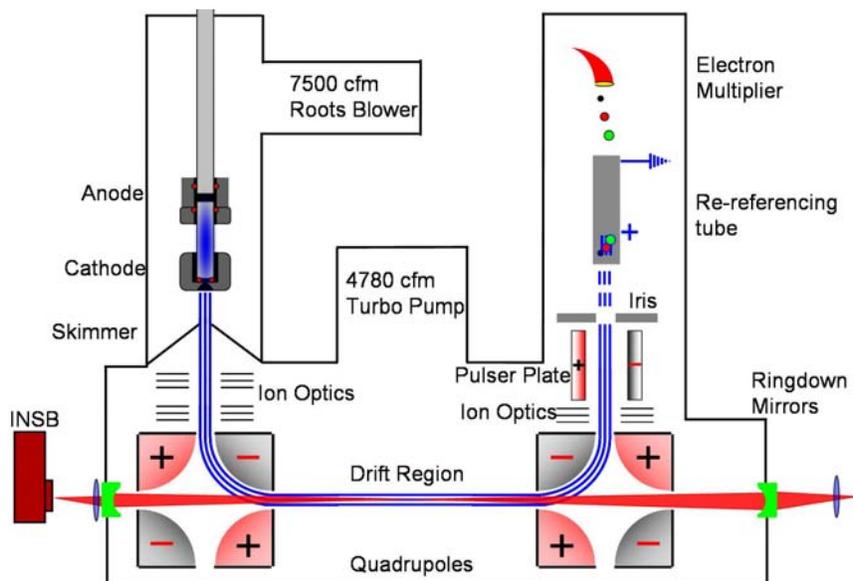


Figure 2 Schematic of SCRIBES instrument. Currently, the source, ion optics, 1st quadrupole, source chamber, ion optics chamber and high finesse ringdown cavity have been constructed. The 2nd quadrupole and mass spectrometer are being designed. The differential pumping needs to be planned and implemented.

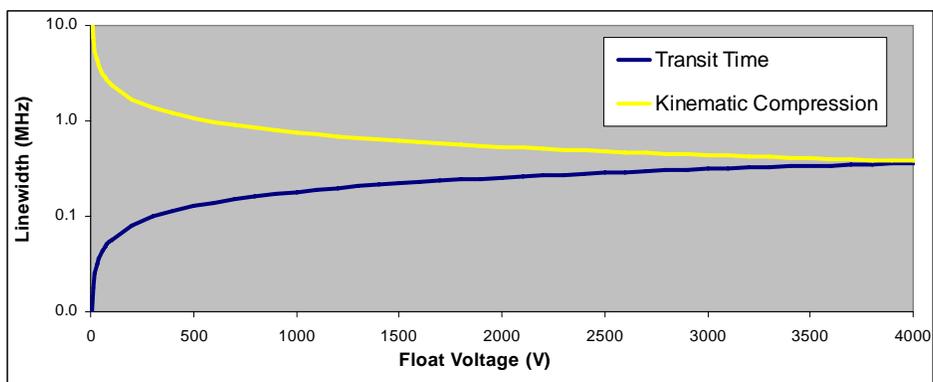


Figure 3 Linewidth reduction from kinematic compression and transit-time broadening linewidths for $C_3H_3^+$ created at 1000 K. 1000 K was chosen to be representative of the plasma temperature.

2 – 5 μm DFG System

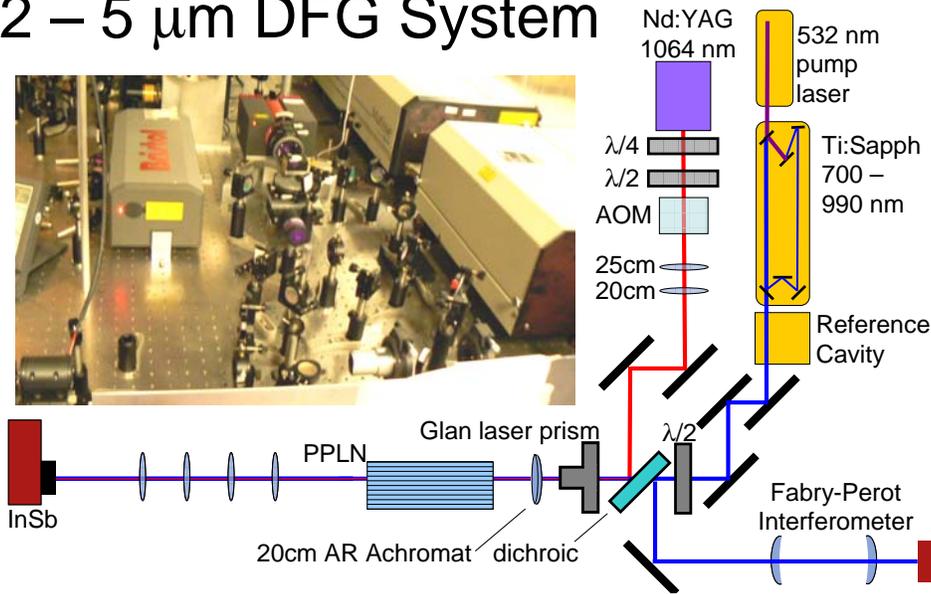


Figure 4 DFG setup. A tunable cw-Ti:Sapph ring laser is coupled with a cw-Nd:YAG, which is modulated by an acousto-optic modulator, and two lenses match the waist of the YAG to the same size and location as that of the Ti:Sapph. The lasers are made co-linear over several meters, and passed through a broadband anti-reflection coated achromat doublet before entering a temperature regulated periodically-poled lithium niobate crystal. Mode matching optics map the IR light to a high-finesse cavity (not shown), and the light is detected by a LN₂ cooled InSb detector.

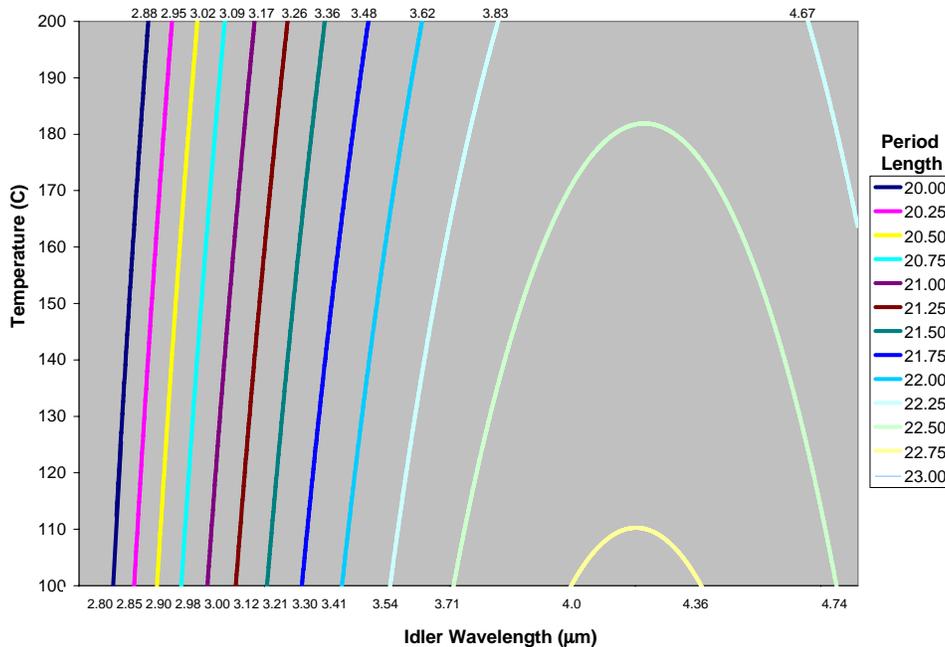


Figure 5 Temperature necessary to satisfy the phase matching conditions for difference frequency generation in a periodically poled lithium niobate crystal using cw Ti:Sapph and Nd:YAG radiation.

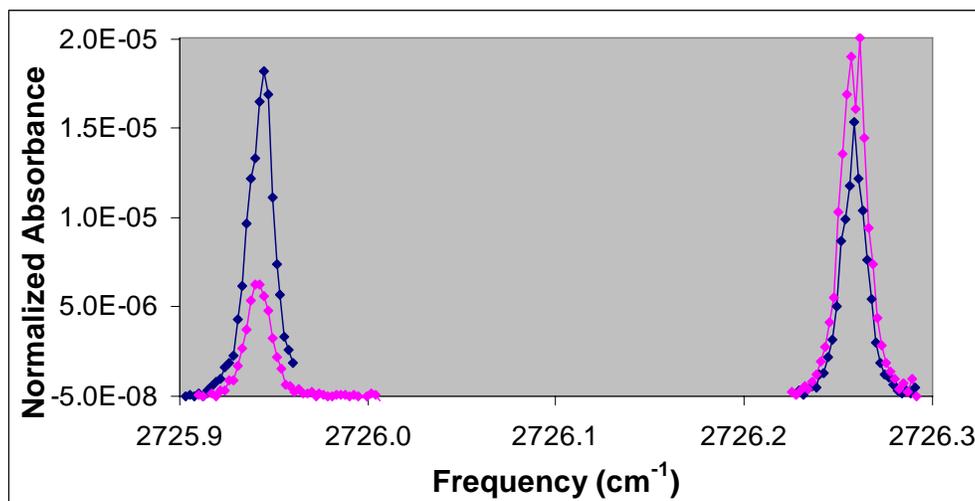


Figure 6 The cw-CRDS spectrum⁴⁰ of H_3^+ in a pulsed supersonic discharge source. The absorbance is normalized to the source current to account for variations, and to the transition moment for each transition. The blue trace is found when normal hydrogen (3:1 ortho:para) is used. The magenta trace is found when para-enriched hydrogen is used. The lower frequency peak is the ortho peak, the higher frequency is the para peak. The step size is 70 MHz, and the FWHM is on the order of 600 MHz.

	C_3H_3^+	H_3^+	N_2^+	
Molecular Mass	39	3	28	g/mol
Temperature	25	1000	1000	K
Beam Current	5	5	5	A
Beam Diameter	3	3	3	mm
Float Voltage	1000	1000	1000	V
Velocity	70291	252619	82997	m/s
Cavity Length	1.15	1.15	1.15	m
Overlap Length	0.46	0.46	0.46	m
Band Strength	175	139	3943	km/mol
Fraction of Band	0.02	0.05	0.006	
Linewidth	5.0E+06	5.0E+06	5.0E+06	Hz
Linewidth	0.00017	0.00017	0.00017	cm^{-1}
Ion Density	6.3E+07	1.7E+07	5.3E+07	ions cm^{-3}
Depth of Transition	4.9E-06	2.8E-06	2.7E-05	
Alpha Min	2.0E-09	2.0E-09	2.0E-09	cm^{-1}
Instrument noise	2.3E-07	2.3E-07	2.3E-07	
S/N	21	12	119	

Figure 7 Sensitivity calculations for C_3H_3^+ , H_3^+ , and N_2^+ , based on a 5 μA beam current collimated to 3 mm diameter at 1000 V beam voltage. Band strengths were calculated *ab initio* (C_3H_3^+), from measured dipole moments of transition (H_3^+) or from measured Einstein A coefficients (N_2^+). The fraction of band is the intensity of the deepest transition divided by the total intensity in the band, yielding an approximate strength of a transition.

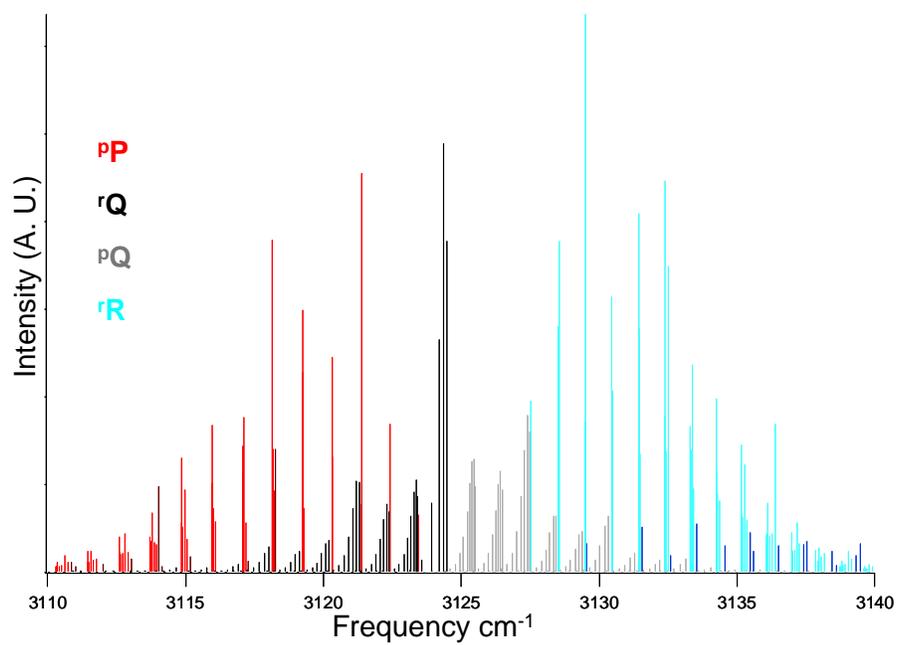


Figure 8 Simulated spectrum of $C_3H_3^+$ at 25 K using Pgopher, with the adopted molecular constants: $B=1.0254$, $C=0.5127$, $\nu_4=3125\text{ cm}^{-1}$ and $\zeta=0.1141$.

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